SIMULATION OF THE LIQUID-LIQUID COEXISTENCE OF THE TETRAHYDROFURAN+WATER MIXTURE IN THE GIBBS ENSEMBLE

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Abstract:

Liquid-liquid coexistence of the tetrahydrofuran (THF) + water (W) mixture was simulated in the NPT Gibbs ensemble (GE). Chemical equilibration of the two phases was provided by the transfer of molecules of each species between the two simulated boxes. To reproduce the experimental data on the THF+W liquid-liquid coexistence the electrostatic interactions between THF and W molecules has to be enhanced with respect to describing the pure substances. The simulated coexistence curve so obtained matches approximately the localization and the shape of the immiscibility region, including the upper critical solution point (UCSP). The analysis of the pair distribution functions (PDFs) emphasizes the role played by the structural changes experienced by the W-W and THF-W interactions between the two coexisting phases.

This study shows that it is possible to simulate in the Gibbs ensemble the liquid-liquid phase separation in aqueous solutions, a promising fact for the understanding of the intimate mechanisms at the origin of the demixing and for the improvement of the intermolecular potentials implemented in computer simulations.

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I. Introduction

Understanding the microscopic origin of the ordering processes in the aqueous solutions is of great importance for many biological and industrial processes. The liquid-liquid phase separation is the simplest example of the temperature induced ordering process. Some aqueous solutions possess a lower critical solution point (LCSP) in addition to the upper critical solution point UCSP [1]. It results in a closed-loop for the phase diagram in the temperature-concentration representation. Moreover, these phase diagrams are amazingly sensible to tiny variations of the molecular structure (deuteration, addition of salts, etc. [1]).

The existence of the UCSP is commonly explained by the changes of the solution structure with the temperature, that allow macroscopic entropy to decrease under cooling (appearance of the two phases instead of one). The first explanation of the LCSP was proposed in the thirties [2]. It is based on the assumption, that the breakdown of the hydrogen bonds (H-bonds) between unlike molecules is responsible for the demixing of the solution above the LCSP. This explanation was widely used to reproduce the closed-loop phase diagrams in lattice models [3,4] and recently to investigate the square-well associating fluids in the Gibbs ensemble [5]. However these models are far from giving a clear relation between microscopic structure of the aqueous solution and its phase behaviour. For example, the main assumption of these models, that H-bonds between solute and water molecules break at the LCSP, contradicts the experimental investigations about the strength of the water-solute H-bonds in aqueous solutions [6]. Besides, the shift of the USCP and LSCP upon small variations of the molecular interactions [1] can not be easily explained in the framework of such models (see [7] for a detailed analysis). In this context simulation studies can shed some light on the

microscopic processes at the origin of the demixing in aqueous solutions.

The THF+W mixture was chosen for investigation because it possesses a closed-loop phase diagram with T_{LCSP}= 345.0 K and T_{UCSP}= 410.3 K [8]. The miscibility gap spreads a little upon deuteration of water molecules (T_{LCSP}= 336.9 K and T_{UCSP}= 416.9 K [9]), and it shrinks completely upon further deuteration of the THF molecules [10,11]. Such sharp changes of the phase diagram of the THF+W mixture upon slight variations of the molecular structure makes it especially relevant for the present study.

The simulation in the Gibbs ensemble GE [12] was chosen to evaluate the liquid-liquid coexistence curve of the THF+W system. Despite the difficulties, connected with the necessity to swap molecules of different sizes between two dense phases, this method is the most direct and convenient way to simulate phase equilibria in liquid mixtures.

II. Simulation of the liquid-liquid coexistence in the Gibbs ensemble

The THF+W liquid-liquid coexistence was evaluated in the NPT Gibbs ensemble [12] at P = 1 bar in the temperature range from 300 K to 425 K. The two coexisting phases were simulated in using two independent cubic boxes with periodic boundary conditions applied in the three dimensions. The TIP4P model for water [13] and a five-site model for THF [14] were used. The Lorentz-Berthelot rules were used for the Lennard-Jones (L-J) interactions. The cutoff radius for the intermolecular interactions was equal to 8 A, and long-range corrections were added for L-J interactions only. The initial configurations of the system were prepared by equilibrating the THF+W mixture at various concentrations in the canonical NPT ensemble. The mole fraction of the THF molecules for the initial configurations varied from 0.0 to 1.0.

The main problem in a Gibbs ensemble simulation is the extremely low probability of the molecular transfers between two liquid phases. This problem becomes still more difficult for hydrogen-bonded liquids at low temperatures and composed of very unlike molecules (e.g. THF and W). The simulation of the THF+W mixture combined all these features and consequently, a major improvement of the efficiency of the molecular transfers have to be achieved.

The rate of molecule deletion was improved by choosing the loosely bound molecules in the simulation box. It means, that only the molecules with an interaction energy higher than some value U_C , were chosen for the transfer. Such biased procedure supposes to correct the acceptance probability of the molecular transfer by a factor P_C, equal to the probability to find at random a molecule with an energy $U > U_C$ in the simulation box. To do so the energy distribution was calculated along the Monte Carlo (MC) run. As far as the correction factor $P_C(X)$ depends on the mole fraction X of the THF molecules, it may vary during the equilibration run in the Gibbs ensemble. Its accuracy was improved by doing rolling averages during the simulation.

The effectiveness of the molecule insertion was improved by early rejection of the new configuration if at least one of the interatomic distances between the inserted molecule and the molecules of the simulation box is shorter than some reference value. These reference values (one for each site-site interaction) were deduced from the calculations of all atomic pair distribution functions associated with the THF+W mixture. In practice these PDF`s were obtained from standard MC simulations at various T and X, and the reference values are identified to the shortest possible distances observed during these MC runs. Hence, with this procedure the early rejection of the insertion attempt gives rise to a negligible bias and no correction is needed for

this attempt.

In summary, one step in the Gibbs ensemble simulation includes the following sequence: 1000 MC moves (rotation and displacement) in both boxes (acceptance probability 40-50%); 2 attempts to vary the volume of each box in order to keep the pressure constant at P = 1 bar (acceptance probability 40-50%); between 10^4 and 10^6 attempts to transfer water molecules or between $5*10^5$ and $1.5*10^6$ attempts to transfer THF molecules, the total probability of acceptance at the end of this sequence being 30÷50%. Notice that each evaluation presented in the following were obtained after several thousands of successful transfers.

III. Simulation results

In Fig.1.1 two equilibration runs of the liquid-liquid coexistence for the THF+W mixture at T = 375 K and P = 1 bar in the Gibbs ensemble are presented. The curves **1a** correspond initially to pure THF (N_{THF}= 145) in one box and pure water (N_W= 512) in the other box, while the curves **1b** to initial mixtures with X_1= 0.125 (N_{THF}= 64, N_W= 448) and X_2= 0.199 (N_{THF}= 102, N_W= 410), respectively. In both runs a strong demixing of the THF+W mixture is observed, and so whatever are the initial concentrations. However the final concentrations of the coexisting phases (X_1= 0.671 and X_2= 0.016) are far from those observed experimentally, namely X_1 = 0.390 and X_2 = 0.090, respectively. This result is not surprising in considering first, the uncertainties about the intermolecular potentials, especially for the cross interactions, and next, the extreme sensitivity of the demixing to deuteration, for example. In order to get closer to the experimental data, we have corrected the Coulombic interactions between THF and W molecules by introducing a corrective factor C. It means that when a THF molecule

interacts with a water molecule its dipole moment is modified by a factor C (C > 1 leads to an enhanced dipole with respect to the original value μ(THF) = 1.92 A [14]). For illustration, the simulation runs performed with the corrective factors C = 1.2 and C = 1.3 are presented in Fig1.2 (curves 2a and 2b, respectively). As expected, the changes are important and point out a possible agreement with experiment (for C = 1.1÷1.2).

The factor C = 1.2 was chosen for the subsequent simulations of the liquid-liquid coexistence at other temperatures. The final results for the coexistence curve are presented in Table 1 and illustrated in Fig.2.

Complete mixing takes place between 385 K and 400 K for a critical concentration very close to the observed one (the critical parameters at the UCSP were estimated by fitting the simulated points to an Ising-type critical behaviour, see Fig.2). At lower temperatures the coexistence curve spreads out and exhibits its maximum width in the temperature range around 325 K. At 300 K a slight tendency to re-mixing may be noted, but this must be considered with caution because at this temperature only the transfer of water molecules was effective during the simulation run.

As for the comparison between simulated and experimental data it must be considered with some care. Although the simulated coexistence curve fits the observed one only approximately, the deviation can be explained by identifying several sources of uncertainties. First of all our simulations were performed at a constant pressure of 1 bar, whereas the experiment shown in Fig.2 was done at a saturated vapour pressure, in other words the pressure varies between 1 bar and 5 bar from the LCSP to the UCSP. In knowing that experimentally the closed-loop shrinks completely in increasing the pressure up to 250 bar [15], this may suggest why the temperature range covered by the miscibility gap is larger for the simulation than for the experiment. In addition to that

the TIP4P model which describes the water-water interactions is not free from inaccuracies (e.g. T_C^{TIP4P} = 580 K [16] instead of T_c^{exp} = 647 K) and can be at the origin of the low temperature shift of the closed loop. Finally, one must bear in mind that the width of the simulated coexistence curve is strongly dependent on the value of the correction factor C (see Fig.1) and that a slight change of its value (here C = 1.2) can have a large effect on the phase diagram. So, in this context and for a first attempt at a simulation of the liquid-liquid coexistence in an aqueous solution, the results presented here describe satisfactorily the very essence of the phenomenon.

IV. Structural properties of the THF+W mixture in one- and two-phases regions

In order to study the structural properties of the coexisting phases and their evolution with the temperature, the pair distribution functions were calculated in the NPT ensemble in using as input data the concentrations of the coexisting phases given in Table 1. In addition other one-phase systems were analyzed: a mixture at the critical concentration and T = 400 K (system 2, Table 1), and an hypothetical mixture with the same concentration but at T = 300 K (system 8, Table 1).

The PDF´s Cen(THF) - O(W) between the geometrical center of the THF molecules and the oxygen of the water molecules are presented in Fig.3. The first maximum characterizes the H-bonds between the THF and W molecules and together with the second maximum it forms the first hydration shell of W molecules around a THF molecule. The number N_H of water molecules H-bonded with a THF molecule (integration up to the first minimum), and the number N_I of water molecules in the first hydration shell (integration up to the second minimum) are both presented in the Table 1

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Notice that, in general, N_H lies between 1 and 2 which means that on average one or two molecules are H-bonded to the oxygen atom of the THF molecule. As for N_I, its value is much larger than N_H because it corresponds to the packing of the water molecules around a THF molecule, a value which is all the more large than the investigated phase is water-rich (e.g. N_I = 21.2 in the water-rich phase of system 1 in Table 1 as compared with N_I = 1.8 in the THF-rich phase of the same system, notice also that N_I = 28 in THF clathrate [17]).

For more details, the PDF`s O(THF) - H(W) are presented in Fig.4. The signature of the O...H-O hydrogen bonds between THF and water molecules is patent in all investigated systems (see the first peak around 1.8 A). The number of these H-bonds varies very little in the THF-rich phase between 300 and 400 K, but decreases more significantly in the water-rich phase (see N_H in Table 1).

The analysis of the water structure was done using the PDF`s O(W) - O(W) (Fig.5). In the mixtures the tetrahedral structure between water molecules, as revealed by the second peak around 4.5 A in Fig.5, seems to persist at higher temperature than in pure water (see the evolution with temperature of the curves 1b,c and 2b,c and compare with the curves 1d and 2d for pure water). Presumably this effect is induced by the presence of THF-W hydrogen bonds in the mixture.

V. Discussion

One of the main goals of this paper was to show the possibility to evaluate by molecular simulation the liquid-liquid coexistence of an aqueous solution (THF+W), and it seems to be achieved. But to do so, in dealing within the framework of the Gibbs ensemble, it has been necessary to improve significantly (by, at least, two orders of

magnitude) the efficiency of the molecular transfers between the coexisting phases. Nevertheless calculations of such kind remain very time consuming. The typical duration of an equilibration run for the demixing of the THF+W mixture is several months on a PC (5÷7 months for each of the results presented in Fig.1).

An important point raises by the present study is the level of accuracy required from the intermolecular potentials to describe even qualitatively the liquid-liquid coexistence curve of the THF+W mixture. Thus the high sensitivity of the simulated coexisting phases to slight changes of the intermolecular force field agrees rather well with the high sensitivity of the observed miscibility gap to subtle variations of the molecular structure induced by a deuteration process or by the pressure [1]. In particular the shrinking of the miscibility gap when increasing the strength of the THF-water H-bonds, is an important result of the simulation.

The analysis of the structure of the THF+W solutions evidences the stability of the O(THF)...H-O(W) hydrogen bonds with the temperature, all over the coexistence range, in contrast with the behaviour of H-bonds in bulk water. These bonds subsist without significant weakening even at the UCSP, which suggests that models of the literature postulating the breakdown of the H-bonds between solute and water molecules above the LCSP [2-5] are too simplistic in the case of aqueous solutions. Moreover the structure analysis also indicates (see Table 1) that the number N_H of water molecules, H-bonded to the oxygen atom of a THF molecule, is significantly higher in the water-rich phase than in the THF-rich phase. This fact may suggest a possible origin of the demixing process above the LCSP. As matter of fact, due to the equality of the Gibbs free energy between the two coexisting phases, the phase with the lowest internal energy has to be balanced by the lowest entropy value and the one with the highest energy has

to produce a larger entropy. In the present case we know that at a given temperature along the coexistence range the energy of the water-rich phase is lower than that of the THF-rich phase (see Table 1 and also [18]). So the entropy of the water-rich phase has to be lower than that of the THF-rich phase. In fact the low entropy of the water-rich phase is the result at once of the orientational order generated by the THF-water H-bonds and of the clathrate-like structure adopted by the other water molecules which surround the THF molecule.

In summary, the present simulation data suggest that the temperature favors the demixing between a more ordered water-rich phase and a less ordered THF-rich phase, the ability of the water molecules to encapsulate the THF ones playing the leading role.

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FIGURE CAPTIONS

Fig.1 The processes of the equilibration of the THF+W mixtures in the Gibbs

ensemble. **1.** Without corrections of the THF-W interactions and with different initial concentrations of the coexisting phases (**a** and **b**). **2.** With correction of the THF-W Coulombic interaction by a factor C=1.2 (**a**) and C=1.3 (**b**). Dotted lines indicate experimental concentrations of the coexisting phases [8].

Fig.2 The coexistence curve of the THF+W mixture. Open circles - experimental data [9]. Closed symbols - simulated points (squares: C = 1.0; circles: C = 1.2). Dotted line - fit of the simulated points to Ising critical behaviour near the UCSP.

Fig.3 The PDF`s Cen(THF)-O(W) for the different THF+W phases. **1**. THF-rich phases and one-phase systems: T = 375 K, C = 1.0 (solid line); T = 400 K, C = 1.2 (dotted line); T = 375 K, C = 1.2 (dashed line); T = 300 K, C = 1.2 (long-dashed line); T = 325 K, C = 1.2 (dot-dashed line). **2**. Water-rich phases: T = 375 K, C = 1.2 (solid line); T = 375 K , C = 1.0 (dotted line); T = 325 K, C = 1.2 (dashed line).

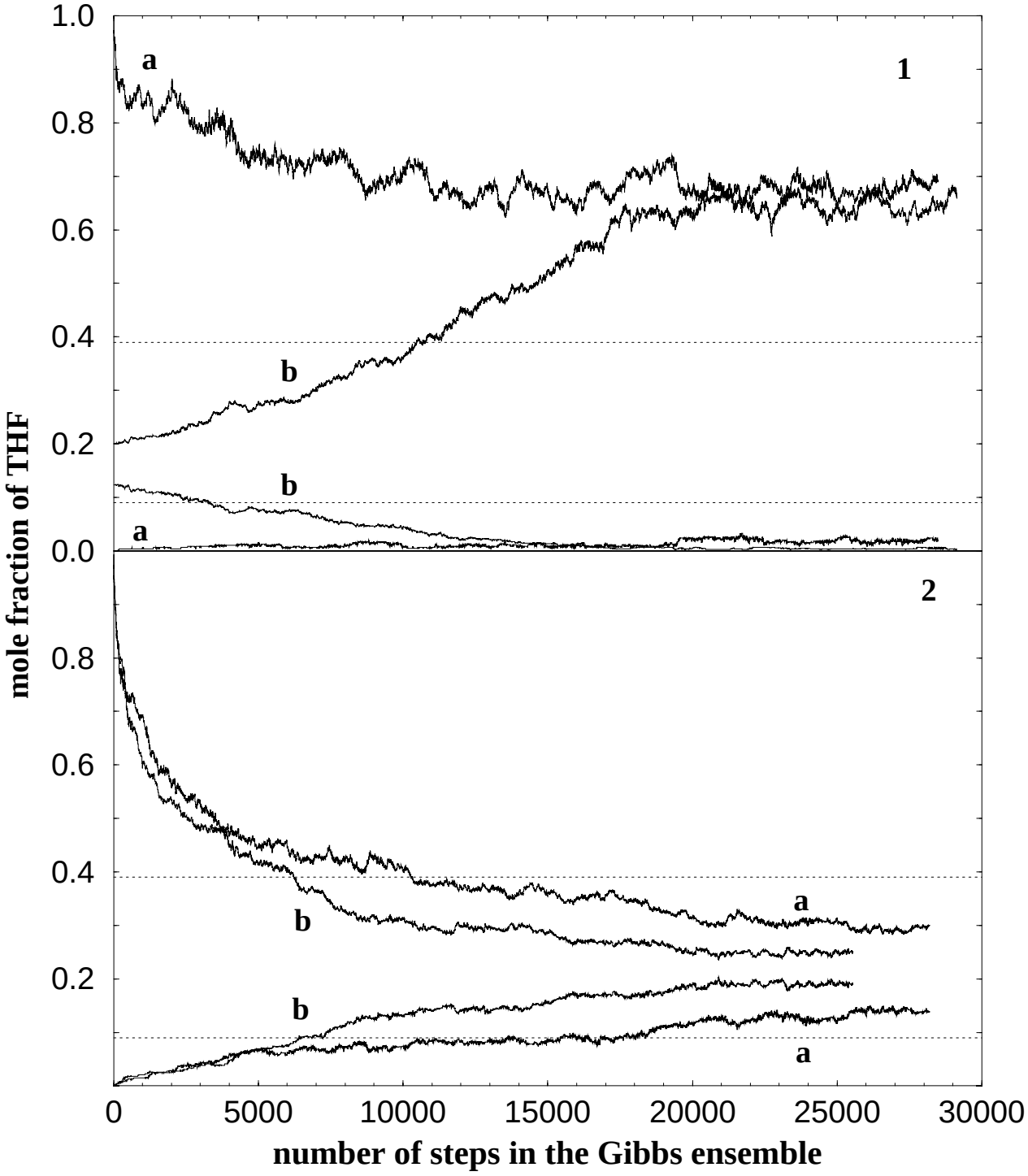
Fig.4 The PDF`s O(THF)-H(W) for the different THF+W phases. The presentation is as in Fig.3.

Fig.5 The PDF`s O(W)-O(W) for the different THF+W phases and bulk water. T = 300 K, C = 1.2 (**1a**); T = 325 K, C = 1.2, THF-rich phase (**1b**), water-rich phase (**1c**); T = 300 K, bulk water (**1d**); T = 400 K, C = 1.2 (**2a**); T = 375 K, C = 1.2, THF-rich phase (**2b**), water-rich phase (**2c**); T = 375 K, bulk water (**2d**).The curves are shifted vertically by 0.15.

Table 1. The parameters of the simulated THF+W phases. **X** - mole fraction of THF; **ρ** - density in g/cm^3; **C** - correction factor for the THF-W Coulombic interactions; **U** - energy of interaction per molecule in kcal/mol; $\mathbf{N_H}$ - calculated number of water

molecules H-bonded with a THF molecule; $\mathbf{N_I}$ - calculated number of water molecules in the first hydration shell of a THF molecule. Numbers in parentheses indicate the uncertainties on the last digits.

system	T, K	phase	X	ρ	U	N_H	N_I
1 (C=1.0)	375	1	0.671(24)	0.788(20)	-6.63(15)	0.3	1.8
		2	0.016(6)	0.917(16)	-8.89(9)	1.8	21.2
2 (C=1.2)	400	1	0.213	0.845(14)	-8.03(11)	1.4	10.1
3 (C=1.2)	385	1	0.277(10)	0.843(14)	-8.16(11)	-	-
		2	0.152(9)	0.871(16)	-8.48(12)	-	-
4 (C=1.2)	375	1	0.303(9)	0.851(15)	-8.30(13)	1.3	8.8
		2	0.129(9)	0.886(18)	-8.67(12)	1.6	11.9
5 (C=1.2)	350	1	0.333(9)	0.858(18)	-8.59(10)	-	-
		2	0.110(7)	0.930(14)	-9.25(9)	-	-
6 (C=1.2)	325	1	0.369(5)	0.912(11)	-9.08(10)	1.4	8.5
		2	0.085(2)	0.973(13)	-9.62(10)	2.1	18.5
7 (C=1.2)	300	1	0.363(2)	0.931(7)	-9.47(7)	-	-
		2	0.086(1)	0.984(11)	-9.94(7)	-	-
8 (C=1.2)	300	1	0.213	0.951(10)	-9.68(8)	1.6	12.2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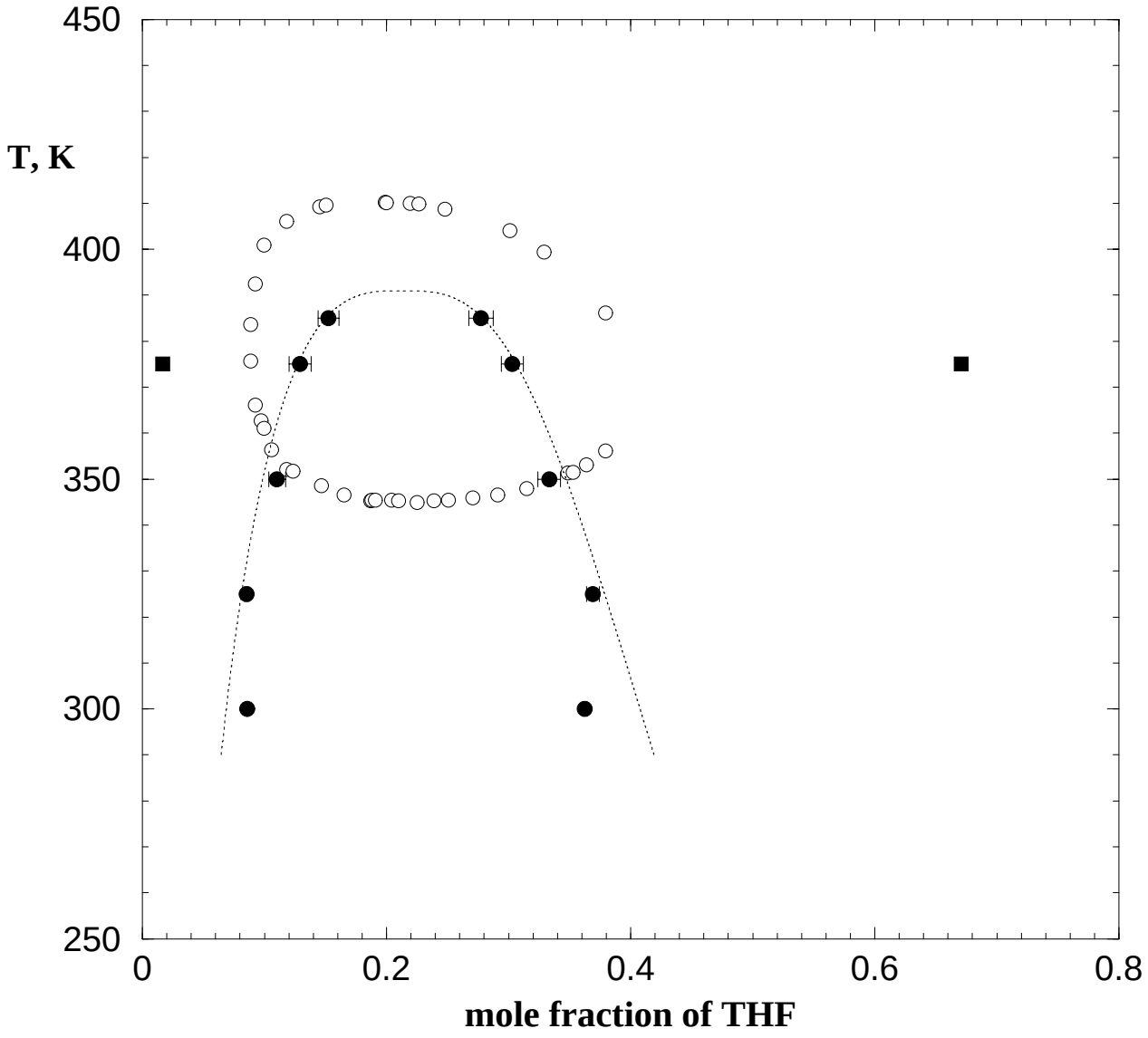
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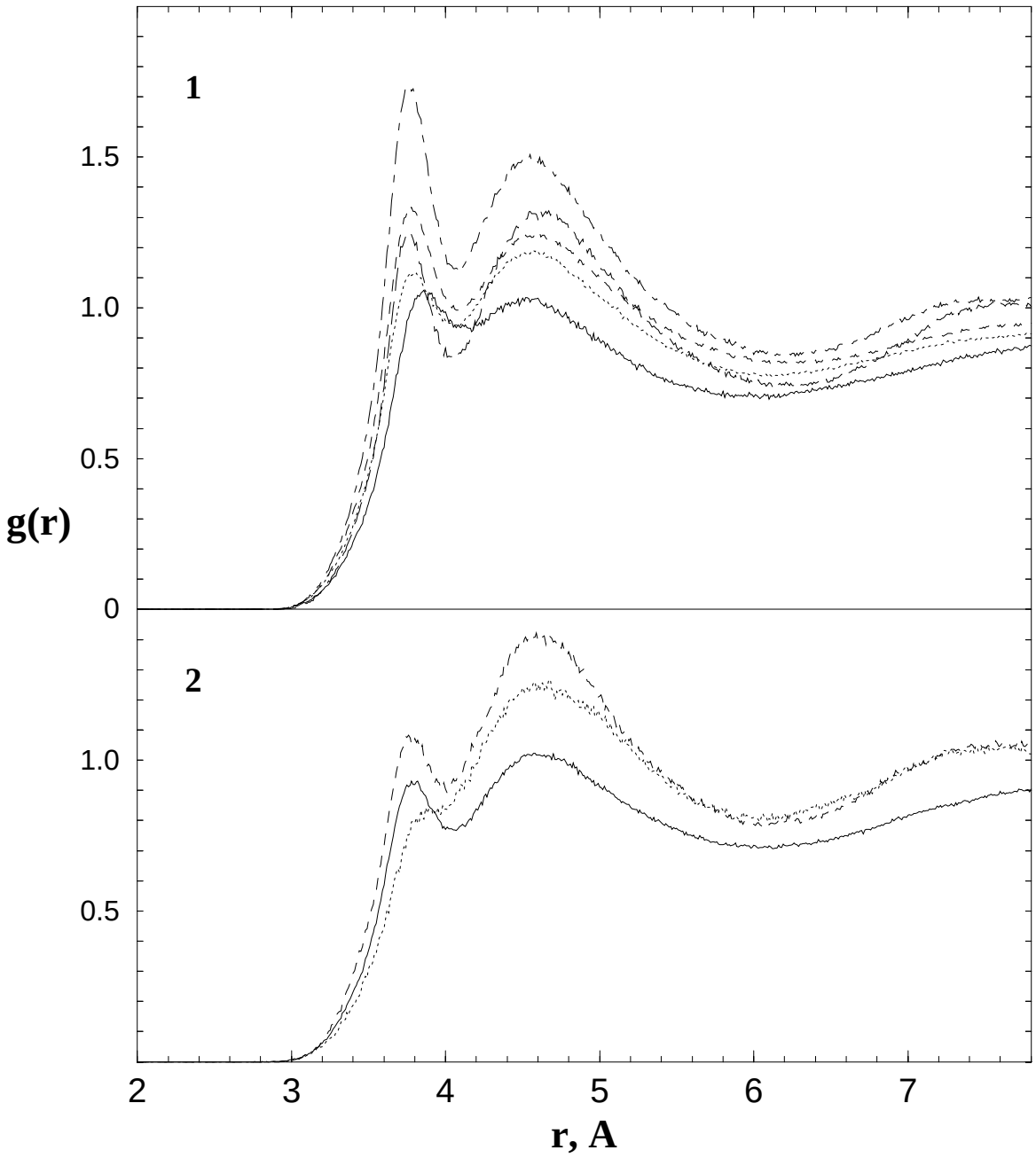
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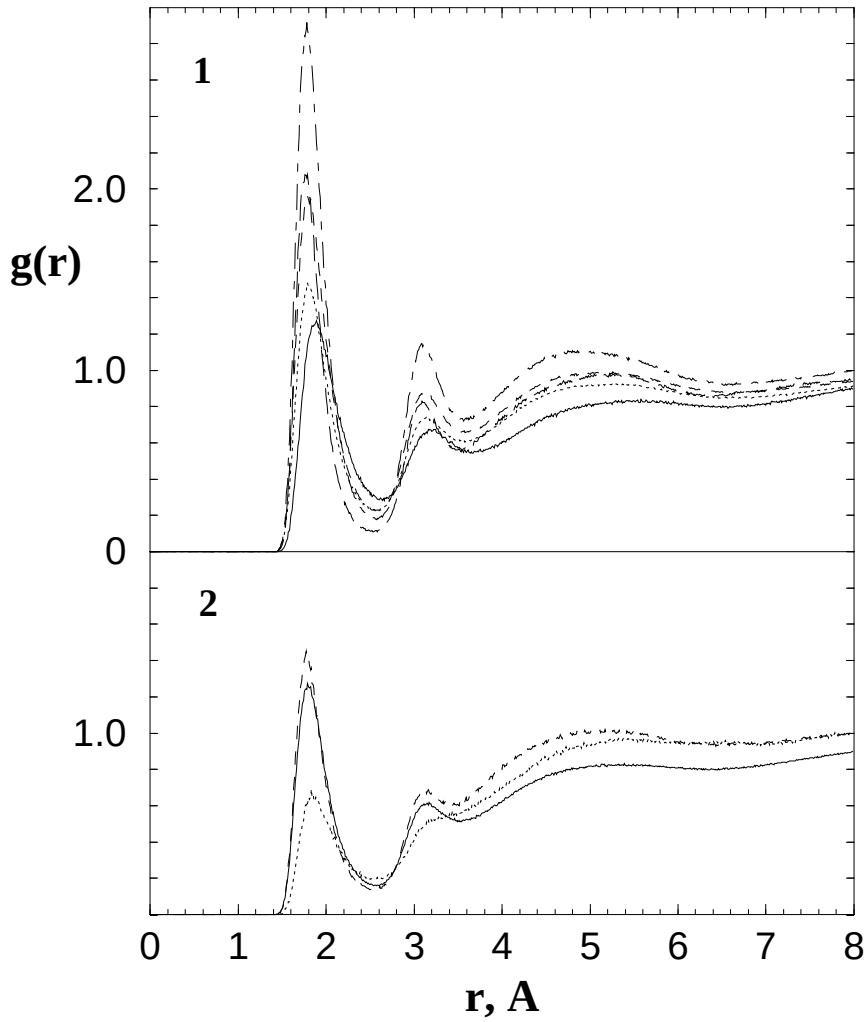
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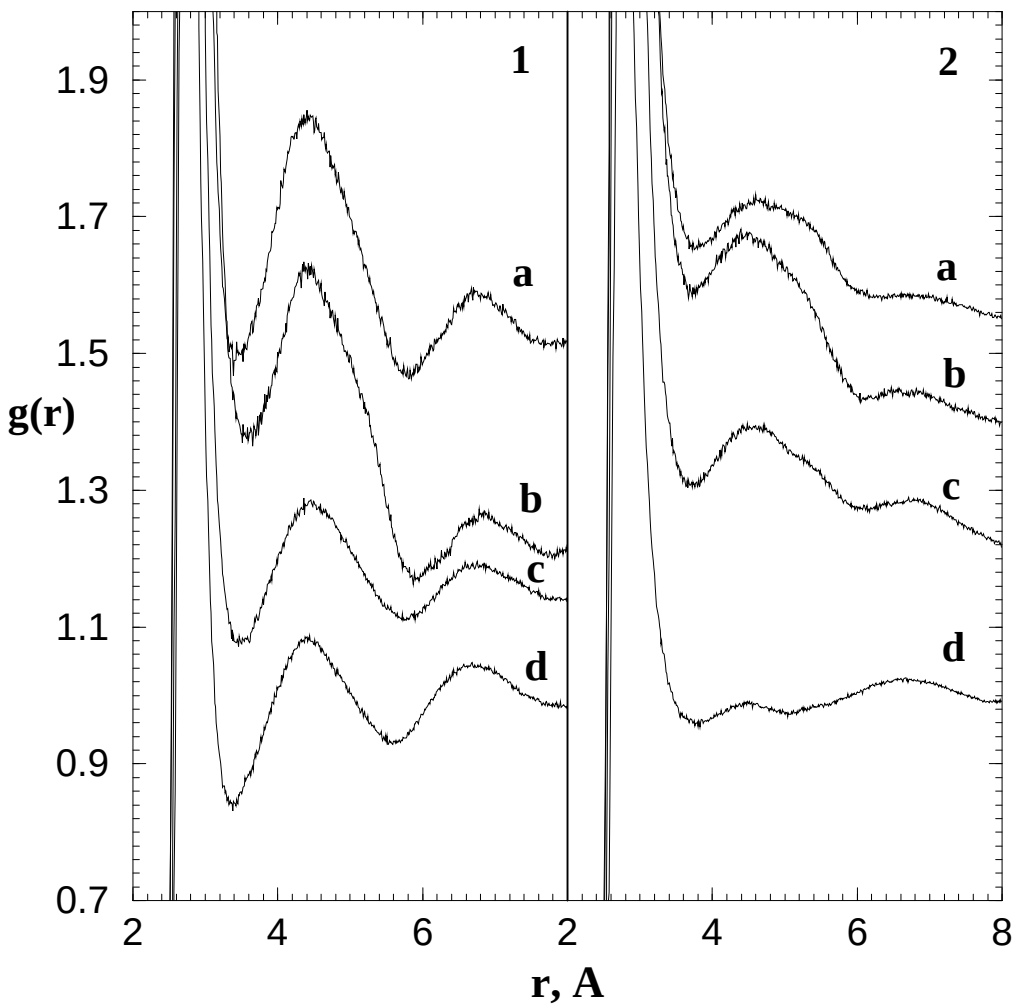
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